

BASE-COAT IN-MOLD COATING

BACKGROUND INFORMATION

[0001] The present invention relates to fiber-reinforced plastic (FRP) bearing thereon a composition that is suitable as a base coat in compression molding applications.

[0002] In-mold coating (IMC) compositions can be applied to FRP to provide a smooth surface and to reduce or eliminate substrate porosity. However, such coatings generally require painting to yield desirable end use properties.

[0003] A typical IMC composition involves the reaction product of an unsaturated fumarate polyester diol, a saturated polyester diol flexibilizer, a crosslinking aliphatic polyol having from 3 to 6 hydroxyl groups, a diisocyanate, and an ethylenically unsaturated crosslinking compound such as styrene; see, e.g., U.S. Pat. Nos. 4,189,517 and 4,222,929.

[0004] Other approaches are described in, for example, U.S. Pat. Nos. 4,331,735, 4,414,173, 4,515,710, and 5,084,353.

SUMMARY OF THE INVENTION

[0005] The present invention provides a coating composition made from compounds that include a saturated polyester urethane acrylate and a saturated hydroxyalkyl (meth)acrylate. Inclusion of a polyacrylate ester of an alkylene polyol and a vinyl-substituted aromatic compound have been found to impart improved properties such as hardness, water resistance, low shrinkage, and adhesion to coatings made from such compositions. Optionally, a saturated (cyclo)aliphatic (meth)acrylate, which is thought to improve the flexibility of the coating, may be added, as well as one or more crosslinking agents.

[0006] The above components can be reacted in the presence of a peroxide initiator to chain extend and form a thermoset resin coating. The cured resin is clear unless pigmented. The present invention may be used as a finish coating in some applications, but the addition of a clear finish coat on its surface can be used to, e.g., enhance gloss. If a clear coating is not desired, various pigments, colorants, etc., can be added to yield a desired end color and opacity.

[0007] In the coating composition, certain compounds and resins, especially aromatic compounds such as aromatic polyesters and/or polyether urethane intermediates, aromatic epoxy-based resins, and the like, are avoided.

5 DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0008] To achieve paint-like properties and clarity, the coating composition utilizes a saturated aliphatic polyester urethane which contains acrylate groups, generally at the terminal portions of the polymer. The polyester portion may be made from aliphatic dicarboxylic acids or aliphatic anhydrides and glycols. Such materials and their preparation are known and commercially available. The aliphatic dicarboxylic acids and anhydrides generally have from 1 to 15 carbon atoms and are desirably saturated (i.e., free of carbon-to-carbon double bonds) with specific examples including carbonic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, the anhydride counterparts thereof, and the like, with adipic acid generally being preferred. Mixtures of two or more of the foregoing acids can be utilized as well. The polyols generally have from 2 to 15 carbon atoms and are saturated, with specific examples including ethylene glycol, propylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, pentane diol, hexane diol, cyclohexanedimethanol dipropylene glycol, 2,2-dimethyl-1,3-propane diol, diethylene glycol, pinacol, and the like. Preferred glycols include ethylene glycol and neopentyl glycol.

[0009] The saturated aliphatic polyester intermediate generally has a number average molecular weight of from about 1000 to about 5000, and desirably from about 1500 to about 2500.

25 [0010] An aliphatic polyisocyanate can be reacted with the saturated polyester intermediate to form a polyurethane. The aliphatic portion is saturated and has from about 5 to 18 carbon atoms such as isophorone diisocyanate (IPDI), hexamethylene diisocyanate, cyclohexyl diisocyanate, and the like, with isophorone diisocyanate being preferred. The average equivalent ratio of NCO groups to OH end groups of the intermediate is from about 1.5 to about 2.5, desirably from about 1.9 to about 2.1, and preferably about 2.0. Such amounts are generally sufficient to form an isocyanate-terminated polyurethane prepolymer which then can be reacted with a hydroxyalkyl acrylate to form the saturated

polyester urethane containing (meth)acrylate generally at the terminal portions of the polymer chain. The acrylates can generally have a C₂-C₁₀ ester portion such as ethyl, propyl, n-butyl, ethylhexyl, and the like, with ethyl and propyl being preferred. An example of a preferred material is CN963B80 polyester urethane acrylate diluted with 10-30% 1,6-hexanediol diacrylate (Sartomer Co., Inc.; Exton, Pennsylvania).

[0011] Polyester urethane acrylates in which one or both of the polyester precursors and polyisocyanates are unsaturated and/or aromatic preferably are not inasmuch as they may yield a coating with a tendency to yellow and degrade on aging. The polyester urethane acrylates are hence substantially free of such compounds, meaning that they generally contain unsaturated and/or aromatic components in an amount less than 25% (by wt.), desirably less than 10% (by wt.), preferably less than 5% (by wt.), and more preferably none at all, based upon the total weight of such polymer(s). Other compounds or monomers that preferably are avoided in the formation of the polyester urethane acrylates are polyethers and epoxy intermediates inasmuch as the same have been found to negatively affect weathering properties of coatings made therefrom. Thus, the polyurethane intermediate contains, based upon the total weight of the polyester urethane acrylates, less than 50% (by wt.); generally less than 25% (by wt.), preferably less than 10% (by wt.), more preferably less than 5% (by wt.), or none at all of polyether and/or epoxy groups.

[0012] Various compounds or components are utilized to react with the polyester urethane acrylate and form a thermoset resin. One component utilized is one or more hydroxyalkyl (meth)acrylates, wherein the alkyl group can contain from 1 to 10 carbon atoms, preferably from 1 to 5 carbon atoms, such as methyl, ethyl, butyl, etc., with propyl being preferred. The amount of such hydroxyalkyl (meth)acrylates is generally from about 2 to about 20 parts by weight (pbw), desirably from about 4 to about 16 pbw, and preferably from about 6 to about 12 pbw per 100 pbw of the polyester urethane acrylate. These compounds are utilized in addition to the hydroxyalkyl methacrylates that may be utilized to form the polyester urethane acrylate resins.

[0013] Another component is one or more vinyl-substituted aromatic compounds. These preferably contain a total of from 8 to 12 carbon atoms,

examples of which include styrene, α -methyl-styrene, vinyl toluene, t-butyl styrene, and the like, with styrene being preferred. The amount of this component is generally from about 10 to about 100 pbw, desirably from about 30 to about 80 pbw, and preferably from about 45 to about 75 pbw per 100 pbw of polyester urethane acrylate.

[0014] Still another component is a polyacrylate, such as a triacrylate or preferably a diacrylate, ester of an alkylene polyol wherein the polyol has from about 2 to about 30 carbon atoms and preferably from about 2 to about 10 carbon atoms such as ethylene diol, butane diol, and the like. The ester moiety on the ends of the alkylene polyol is generally derived from (meth)acrylic acid or similar unsaturated carboxylic acid. Examples of preferred diacrylate esters of an alkylene diol include triethylene glycol di(meth)acrylate, (di)ethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,3-butylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, (propoxylated) neopentyl glycol di(meth)acrylate, polyethylene glycol (200, 400, 600) di(meth)acrylate, tripropylene glycol diacrylate, and alkoxylated aliphatic diacrylate. Examples of trifunctional acrylate esters of an alkylene polyol which can be optionally utilized include tris(2-hydroxyethyl) isocyanurate tri(meth)acrylate, (alkoxylated) trimethylolpropane tri(meth)acrylate, pentaerythritol triacrylate, and propoxylated glyceryl triacrylate. A preferred polyacrylate ester of an alkylene polyol for use in the present invention is 1,6-hexanediol diacrylate.

[0015] The amount of the diacrylate ester of the alkylene polyol is generally from about 10 to about 40 pbw, desirably from about 15 to about 35 pbw, and preferably from about 20 to about 30 pbw for every 100 pbw of the polyester urethane acrylate. The amount of the optional triacrylate ester of the alkylene polyol is low and generally is less than 10 pbw and preferably less than 5 pbw for every 100 pbw of the polyester urethane acrylate.

[0016] A coating composition derived from ingredients that include the foregoing generally is clear. Alternatively, the coating can be colored by utilizing a pigment, colorant, or the like in an amount to yield a desired color, tint, hue, or opacity. Pigments and pigment dispersions are known to the art and include, for

example, TiO_2 , carbon black, phthalocyanine blue or red, chromium and ferric oxides, and the like.

[0017] The coating composition optionally can contain additional components such as a (cyclo)aliphatic (meth)acrylate wherein the (cyclo)aliphatic portion is 5 saturated and contains from about 1 to about 50 carbon atoms, desirably from about 2 to about 20 carbon atoms. Representative examples include methyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, isodecylmethacrylate, 2(2-ethoxy)ethoxy ethylacrylate, stearyl (meth)acrylate, lauryl (meth)acrylate, glycidyl methacrylate, isodecyl acrylate, isobornyl (meth)acrylate, tridecyl (meth)acrylate, 10 and caprolactone acrylate, with isobornyl acrylate being preferred. The (cyclo)-aliphatic (meth)acrylate, when present, may optionally be added as a monomer diluent for the aliphatic polyester urethane acrylate component. Thus, EbecrylTM 8411 aliphatic urethane diacrylate diluted 20% with isobornyl acrylate monomer (Surface Specialties Inc. of the UCB Group of companies; Smyrna, Georgia). The 15 amount of the saturated (cyclo)aliphatic (meth)acrylate, when present, is generally from about 0.1 to about 25 pbw, desirably from about 0.1 to about 15 pbw, and preferably from about 0.5 to about 10 pbw per 100 total pbw of the polyester urethane acrylate.

[0018] The coating compositions of the present invention can also contain 20 conventional additives, and fillers, etc., in conventional amounts. Thus, various cure inhibitors such as benzoquinone, (methoxy)hydroquinone, p-t-butylcatechol, and the like, can be utilized. Another additive is an accelerator such as cobalt octoate. Other classes of accelerators include zinc, or other metal, carboxylates. Various light stabilizers can be utilized such as, for example, the various hindered 25 amines (HALS), substituted benzophenones, and substituted benztriazoles, and the like. Lubricants and mold release agents are generally utilized with specific examples including various metal stearates, such as zinc stearate or calcium stearate or phosphonic acid esters. Reinforcing fillers such as talc can be utilized. Talc has also been found to help promote adhesion of the in-mold coating 30 composition to the fiber reinforced plastic substrate. Another additive is a hardener and thixotrope such as silica.

[0019] The polyester urethane acrylate and the other curing monomers or components of the present invention are chain extended through the utilization of

a free radical initiator such as a peroxide. Examples of suitable free radical initiators include tertiary butyl perbenzoate, tertiary butyl peroctoate in diallyl phthalate, diacetyl peroxide in dimethyl phthalate, dibenzoyl peroxide, di(p-chlorobenzoyl) peroxide in dibutyl phthalate, di(2,4-dichlorobenzoyl) peroxide in dibutyl phthalate dilauroyl peroxide, methyl ethyl ketone peroxide, cyclohexanone peroxide in dibutyl phthalate, 3,5-dihydroxy-3,4-dimethyl-1,2-dioxacyclopentane, t-butylperoxy(2-ethyl hexanoate), caprylyl peroxide, 2,5-dimethyl-2,5-di(benzoyl peroxy) hexane, 1-hydroxy cyclohexyl hydroperoxide-1, t-butyl peroxy (2-ethyl butyrate), 2,5-dimethyl-2,5-bis(t-butyl peroxy) hexane, cumylhydroperoxide, diacetyl peroxide, t-butyl hydroperoxide, ditertiary butyl peroxide, 3,5-dihydroxy-3,5-dimethyl-1,2-oxacyclopentane, and 1,1-bis(t-butylperoxy)-3,3,5-trimethyl cyclohexane and the like, and mixtures thereof. Another suitable free radical initiator is Luperox™ 575 t-amyl peroxy-2-ethylhexanoate (ATOFINA Chemicals, Inc.; Philadelphia, Pennsylvania).

[0020] Using mixtures of initiators to take advantage of, e.g., their different decomposition rates and times at different temperatures can be desirable. A preferred initiator is t-butyl perbenzoate. The peroxide initiator preferably is used in an amount sufficient to overcome the effect of any inhibitor and to cause curing of the ethylenically unsaturated compounds. In general, the peroxide initiator is used in an amount of from about 0.25 to about 5%, desirably from about 1 to about 4%, and preferably from about 1 to about 2%, by weight based on the total weight of all of the ethylenically unsaturated components employed in the coating compositions. The reaction of the polyester urethane acrylate with the curing components in the presence of the peroxide initiator is generally at a temperature of from about 90° to about 165°C (200°-330°F) and desirably from about 130° to about 155°C (270°-310°F).

[0021] The coating composition can be prepared as follows: the polyester urethane acrylate can be mixed with the vinyl-substituted aromatic compound(s) (e.g., styrene) and the hydroxyalkyl (meth)acrylate (e.g., hydroxypropyl methacrylate) and, if a saturated (cyclo)aliphatic (meth)acrylate such as isobornyl acrylate is included, this component is included in the mixture; after these compounds are mixed, fillers and additives such as cure inhibitors, light stabilizers, lubricants, etc., are added and mixed; the free radical peroxide initiator

typically is added last. (The polyacrylate ester of a polyol is typically present in the polyester urethane acrylate from the supplier.)

[0022] When a coating having a specific color is desired, one or more pigments, colorants, etc., can be utilized in suitable amounts. As known, often 5 times various pigments or colorants are added with a carrier, for example, a polyester, so that they can be easily blended. Any conventional or suitable mixing vessel can be utilized, and the various components and additives mixed until the compounds are blended. Even if pigments are not contained in the blend, the mixture at this point is typically not clear. When desired, the mixed ingredients are 10 coated onto a FRP such as a sheet molded compound as by injection molding with the IMC composition heated to a cure temperature. The cure temperature will vary depending upon the particular curative or peroxide utilized. Suitable cure temperatures generally range from about 90° to about 165°C (200°-330°F).

[0023] Upon cure or chain extension, the coating becomes clear and have 15 very good properties such as high clarity, good adhesion to an FRP substrate such as a sheet molded compound, good hardness (e.g., a pencil hardness of at least H and desirably at least 2H), good scratch resistance, good water resistance, and good UV resistance. Such properties result in a coating which may be suitable as a finished surface in certain applications. However, a clear top coat 20 can be applied to the surface after application of the coating to impart a high gloss to the composite, especially in those applications that demand high gloss finishes, such as automotive and other areas. That is, the coating composition when cured can be utilized as is with regard to some particular end use applications and does not need subsequent surface treatments, e.g., coating, another layer, etc., such 25 as a paint, and the like. Nevertheless, a clear, high gloss top coat is preferred when a high gloss finish is desired.

[0024] The resulting coatings are generally flexible and can be utilized on any surface of a FRP substrate which can be a thermoplastic or a thermoset, on sheet 30 molded compounds which are generally thermosets, on low pressure molding compounds (LPMC), and the like. Suitable end uses of finished or top-coated coating compositions of the present invention include various automotive parts such as spoilers, air dams, truck liners, patio furniture, satellite dishes, water craft components, and the like.

[0025] The invention will be better understood by reference to the following illustrative, non-limiting examples.

EXAMPLES

5 Formulas A and B, set forth below, were mixed and molded as follows:

Formula A

[0026] CN963B80™ polyester urethane acrylate (PUA), diacrylic ester of hexanediol, styrene, isobornyl acrylate and hydroxypropyl methacrylate (HPMA) in the indicated amount were added to a container and mixed thoroughly using 10 mixing procedures conventional for organic resin solutions. Hydroquinone, cobalt octoate (12% in mineral oil), and zinc and calcium stearates were weighed into the resin solution prepared above, and again mixed thoroughly to dissolve the organics and disperse the stearates. Talc and Cab-O-Sil™ fumed silica (Cabot Corp.; Billerica, Massachusetts) were then weighed into the container with the 15 organics and stearates, and mixed thoroughly to disperse the solids. All of the mixing occurred without external heating. A t-butyl perbenzoate initiator was added to the solution prepared above, and mixed thoroughly.

[0027] The FRP molding was prepared in a 40.6 cm × 40.6 cm chromed steel shear-edge mold from a conventional polyester SMC used commercially to 20 prepare exterior automotive body panels. Molding conditions for the SMC were 149°C, a 70-second cure time, and 6.9 MPa pressure.

[0028] The coating was applied immediately following SMC cure by opening the mold, pouring in the coating on the FRP molding, and re-closing the mold. Cure conditions for the IMC were 149°C, a 60-second cure time, and 6.9 MPa 25 pressure.

Formula B

[0029] Same as formula A, with the exception of the addition of isobornyl acrylate and a second aliphatic polyester urethane acrylate (Ebecryl™ 8411).

30 [0030] The formulations set forth below are based on a 600 g coating sample. Thus, the weight values provided below are the amount of each component added to obtain 600 g of the coating and will change if the amount of coating to be

produced is varied. Of course, the weight percent of each component will remain constant regardless of the amount of coating.

Table 1

	FORMULA A		FORMULA B	
	weight %	weight (g)	weight %	weight (g)
CN963B80 PUA	41.72	250.31	39.72	238.32
Ebecryl 8411 PUA	0.00	0.00	2.00	12.00
HPMA	2.86	17.18	2.86	17.18
cobalt octoate	0.39	2.31	0.39	2.34
hydroquinone	0.03	0.17	0.03	0.18
fumed silica	1.35	8.09	1.35	8.10
zinc stearate	0.51	3.08	0.51	3.06
calcium stearate	0.19	1.16	0.19	1014
talc	4.81	28.88	4.81	28.86
styrene	24.07	144.41	24.07	144.42
white paste*	24.07	144.41	24.07	144.42
Total:	100%	600g	100%	600g

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*50% by wt. each of CN963B80 PUA and TiO₂.

[0031] Formulations A and B were tested with regard to various properties such as pencil hardness, tape adhesion and chip resistance. The results of these tests are set forth in Table 2.

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Table 2

Test	Formula A	Formula B
Pencil Hardness	H	H
Tape adhesion (GM9071P)	100%	100%
Cross-hatch tape adhesion (Ford B1 106-1)	0	0
Chip resistance (GM9506P)	9	9

[0032] As apparent from the data of Table 2, coatings made from these compositions exhibit good properties. Addition of Ebecryl™ 8411 PUA (formula B) 15 appears to increase the flexibility of the resulting coating, although the flexibility of the coating from formula A is quite sufficient for most applications.